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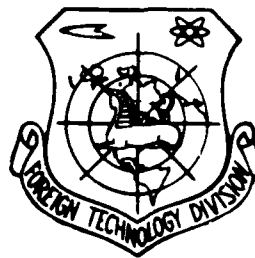
## FOREIGN TECHNOLOGY DIVISION



### STRUCTURAL CHANGES DURING THE OXIDATION OF CHROMIUM YTTRIUM ALLOYS

by

L. M. Kumok, L. N. Larikov, et al.



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## UNEDITED ROUGH DRAFT TRANSLATION

STRUCTURAL CHANGES DURING THE OXIDATION OF  
CHROMIUM YTTRIUM ALLOYS

By: L. M. Kumok, L. N. Larikov, et al.

English pages: 4

SOURCE: AN UkrSSR. Struktura Metallicheskih  
Splavov. (Academy of Sciences of the  
Ukrainian SSR. Structure of Metallic  
Alloys), 1966, pp. 99-104.

Translated by: L. Marokus/TDERO-2

TT8000218

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PREPARED BY:  
TRANSLATION DIVISION  
FOREIGN TECHNOLOGY DIVISION  
WP-APD, ONR.

DATA HANDLING PAGE				
01-ACCESSION NO. TT8000218	02-DOCUMENT LOC	03-TOPIC TAGS metal oxidation, alloy structure, oxidation rate, oxidation kinetics		
04-TITLE STRUCTURAL CHANGES DURING THE OXIDATION OF CHROMIUM YTTRIUM ALLOYS				
05-SUBJECT AREA  11, 20				
06-AUTHOR/CO-AUTHORS KUMOK, L. M.; LARIKOV, L. N.; YATSENKO, T. K.; MAKSIMENKO, YE. A.			07-DATE OF INFO -----66	
08-SOURCE AN UKRSSR. STRUKTURA METALLICHESKIKH SPLAVOV (RUSSIAN)			09-DOCUMENT NO. FTD-HT-23-1259-67	
			10-PROJECT NO. 72301-78	
11-SECURITY AND DOWNGRADING INFORMATION  UNCL, C		12-CONTROL MARKINGS  NONE		13-HEADER CLASS  UNCL
14-REEL/FRAME NO. 1883 1707	15-SUPERSEDES	16-CHANGES	17-GEOGRAPHICAL AREA UR	18-NO. OF PAGES 4
19-CONTRACT NO.	20-REF ACC. NO. AT6036279	21-PUBLISHING DATE	22-TYPE PRODUCT Translation	23-REVISION FREQ None
24-STEP NO. UR/0000/66/000/000/0099/0104		25-ACCESSION NO. TT8000218		
<p>ABSTRACT</p> <p>The oxidation behavior at 1100--1450C of 99.9%-pure chromium and chromium-yttrium alloys containing 0.5, 1.0 or 2.0% yttrium has been studied. It was found that yttrium improves the oxidation resistance of chromium and the oxidation rate of all the alloys tested, especially that of the alloy containing 0.5% yttrium (see Fig. 1), was much lower than that of pure chromium. On all the alloys tested, a dense tightly adhering oxide layer was formed, while the oxide layer on pure chromium easily peeled off. In pure chromium, a certain quantity of chromium oxides and nitrides was formed to a depth of 650 <math>\mu</math> in a metal oxidized at 1450C for 9 hr. In chromium-yttrium alloys, the amount of chromium oxides was much smaller and the nitrides</p>				

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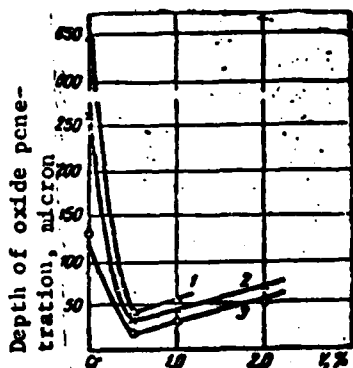


Fig. 1. Dependence of the penetration depth of oxides upon the yttrium concentration

1 —1450C for 9 hr; 2 —1400C for 20 hr;  
3 —1350C for 30 hr.

were absent altogether. The penetration of oxygen and nitrogen into pure chromium proceeds mostly along the grain boundaries. This was not observed in the chromium-yttrium alloys. It is believed that yttrium improves the oxidation resistance of chromium primarily by a refining effect. Orig. art. has: 5 figures.

## STRUCTURAL CHANGES DURING THE OXIDATION OF CHROMIUM YTTRIUM ALLOYS

L. M. Kuzok, L. N. Larikov, et al.

The study of chromium yttrium alloys represents greater practical interest, since these alloys possess a higher plasticity in comparison with initial chromium [1]. There are indications of their higher resistance to oxidation [2, 3].

The purpose of this operation was the study of laws of the oxidation process of chromium alloys with various yttrium constant during heating in the air at high temperatures. Initial electrolytical chromium, refined in hydrogen (99.9%) and its alloys with 0.5, 1.0 and 2.0% Y were submitted to us authors of report [1], where are also described the conditions of their preparation. The heating of samples at a temperature range of 1100-1450°C was carried out in silite and molybdenum furnaces in open alundum pipes.

The oxidation kinetics of chromium-yttrium alloys were investigated by the gain in weight of the samples  $\Delta m$  relative to a unit of area. In Fig. 1 are represented results, obtained during the study of chromium alloy with 0.5% of Y. In this drawing are also given comparisons and data, obtained by us during the investigation of pure chromium.

In both instances the oxidation kinetics is well described by a parabolic law

$$\left(\frac{\Delta m}{S}\right)^2 = Kt. \quad (1)$$

An analogous course of the chromium oxidation process has already been described in reports [3, 4] in a range of temperatures of 700-1200°C.

The temperature dependence of the rate of chromium oxidation (Fig. 2) can be described by an exponential law

$$K = K_0 \exp\left(-\frac{E}{RT}\right). \quad (2)$$

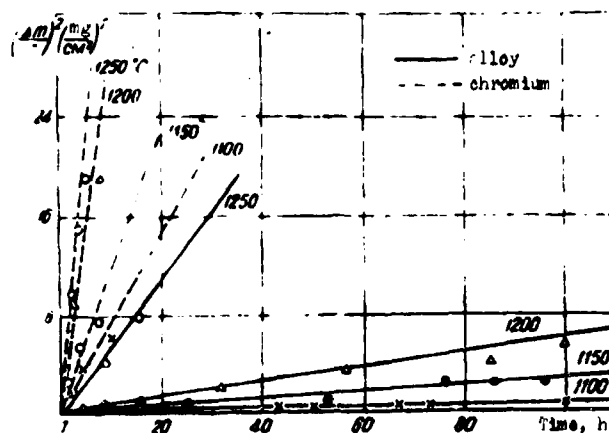


Fig. 1. Dependence of chromium sample gains (-) and its alloy with 0.5% Y(---) upon the annealing time.

Value  $E = 63.5$  kcal/g-atm is quite close to the activation energy of oxygen diffusion in chromium (66.3 kcal/g-atm according to data [4]).

The temperature dependence of the oxidation rate of the chromium yttrium alloy is even more steeper, and differs in this respect between chromium and its alloy, they decrease with a rise in temperature (see Fig. 2).

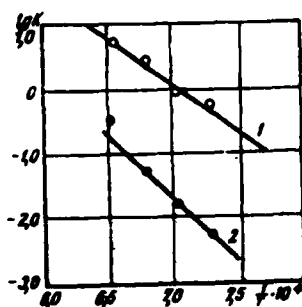


Fig. 2. Temperature dependence of rate of chromium oxidation (1) and its alloys with 0.5% Y (2).

The rate of oxidation of the chromium-yttrium alloy, however, is substantially lesser than the rate of oxidation of initial chromium in the entirely investigated temperature range and annealing time.

Visual investigation has shown, that in chromium-yttrium alloys the surface of the samples is covered by a dense scaling layer in contrast to chromium, in which the scale peels off easily. Substantial differences exist also in the layers under the scale. At a laminar phase analysis, carried out with the aid of X-ray diffractometer URS 50-I it was established, that in the under scale layer of chromium is situated a certain amount of oxides and chromium nitrides up to a considerable depth (650  $\mu$  within 9 hrs at 1450°C). In alloys the interference lines

$\text{Cr}_2\text{O}_3$  is observed to considerably lesser depths, and the lines of nitrides is generally impossible to detect by the indicated method. Figure 3 illustrates the effect of yttrium concentration on the depth of oxygen penetration in the under-scale chromium layer at various temperatures. Most resistant was found to be a chromium alloy with 0.5% Y.

Microstructural investigation has shown, that the structure of the underscale layer in nonalloyed chromium has changed substantially (Fig. 4a). In contrast

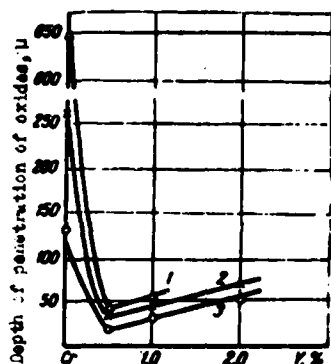


Fig. 3. Dependence of depth of penetration of oxides upon the concentration of yttrium: 1 - 1450°C, 9 hrs; 2 - 1400°C, 20 hrs; 3 - 1350°C, 30 hrs.

layer [2]. The basic difficulty for the explanation of such type of phenomenon is the very low solubility of yttrium in chromium.

to the basic metal it is characterized by very fine grains of higher hardness (Fig. 4). In chromium alloyed with yttrium this effect is absent (Fig. 5). This phenomenon has already been described in report [6], whereby the authors assumed, that the layer of higher hardness is the nitride phase. Thin layers phase analysis carried out by us has, however, not confirmed this conclusion. The basic mass of the subscale layer consists of metallic chromium with separations of oxides and nitrides. The high hardness of the layer is bound, evidently, with the highly dispersion character of these separations.

Many view points do exist with respect to the mechanism of the effect of alloying elements on the scale resistance of chromium. For example, some authors assume, that this effect is connected with the change in composition of the oxide film and suboxide



Fig. 4. Microstructures of oxidized chromium: a - 1450°C, 9 hrs, X 7; b - 1350°C, 20 hrs, X 230; v - ditto, X 400.

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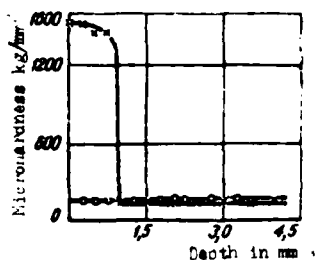


Fig. 5. Change in microhardness by the section of chromium samples (X-X) and its alloy (---) with 1% Y (1450°C, 9 hrs). a - microhardness kg/mm<sup>2</sup>.

The penetration of oxygen and nitrogen into the chromium takes place preferably over the grain boundaries (see Fig. 4b). This effect is absent in chromium-yttrium alloys. The basic effect of yttrium on the mechanical properties of chromium is bound with its refining effect [1]. It is also known, that the preferential penetration of oxygen, taking place over grain boundaries of technical iron, is absent in purified iron [7]. This offers basis to assume, that the protective effect of yttrium on the oxidation of chromium is bound in a considerable degree with its refining action. A certain confirmation of this point of view appears to be the nonmonotonous nature of concentration of the dependence of the protective yttrium effect.

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Submitted  
11 June, 1965